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The influence of laser induced consolidation on the ablation threshold of nanoparticulate ITO-layers

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Abstract

Indium tin oxide (ITO) is one of the few materials, which combines optical transparency in the wavelength range of visible light and electrical conductivity. It offers a wide range of applications in the field of optoelectronic devices such as solar cells or displays. To the present day, ITO is commonly deposited in a vacuum environment. Deposition under vacuum atmosphere is a cost-intensive process and not compatible with modern manufacturing techniques, like roll-to-roll processing. To overcome this limitation we propose the generation of ITO layers by deposition of ITO nanoparticles under atmospheric conditions. For the generation of functional devices structured layers are required. The exact damage threshold of nanoparticulate ITO layers is essential to minimize influence of the structuring process on the substrate. In our measurements we used three different substrates, spin coated layers, annealed layers and consolidated layers.

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Keywords: ITO; Structuring; Damage Threshold; ultra-short pulse laser

1. Introduction

Due to its optical and electrical properties indium tin oxide is used in optoelectronic applications, such as solar cells, displays and optoelectronic devices. Commonly ITO is deposited in vacuum, which is a costly and time-consuming procedure.

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Baum et al. demonstrated the possibility to generate dense films from nanoparticulate layers by laser consolidation under ambient conditions, which is fast, inexpensive and suitable for modern manufacturing techniques like printed electronics. Here, ITO nanoparticulate layers were generated by spin coating (spin coated layer). In the following layers are annealed on a hotplate to remove all organic compounds and to enhance particle-particle contact (annealed layer). To improve the electrical properties the layers are consolidated by laser irradiation (consolidated layer). The obtained-ITO layers can be used in electro-optical applications and in holography. For electrical applications consolidated layers are used since they possess superior conductivity in comparison to non-consolidated layers. In order to generate electrical circuits and devices these layers need to be structured.

For laser structuring, knowledge of the damage threshold of the particle layers is fundamental for the optimization of the structuring process. It allows the generation of minimal structures or minimization of the impairment of the glass substrate. The damage threshold of non-consolidated ITO layers which were mainly generated by vacuum deposition techniques like sputtering has been characterized for different laser systems by various groups. For example, M. Park et al. (2006) investigated the damage threshold of ITO thin films with a thickness of 200 nm for organic light-emitting diode applications generated by vacuum deposition. The damage threshold was determined to be 0.07 J/cm^2. However, layers deposited by vacuum procedures are more homogeneous and not comparable to the nanoparticulate ITO films. The damage threshold of consolidated ITO layers has yet not been documented so far. In this work we show investigations on the damage threshold of unheated, annealed and consolidated layers for fs-laser pulses at a wavelength of 800 nm.

2. Experimental details

In the following we describe the procedure used to generate ITO-layers on a glass substrate.

2.1. ITO nanoink preparation

In our experiments we used ITO particles commercially available by Evonik Industries AG. The particles were put in suspension in absolute ethanol at a 20 % wt loading. The size distribution of the particles in the suspension reaches from 20 nm to 120 nm. Agglomeration of the particles was prevented by the organic agent 2-[2-(2-methoxy-ethoxy)ethoxy]acetic. M. Mahajeri et al. (2012) in detail describes the production of the suspension.

2.2. Layer deposition and treatment

The layer preparation is divided into three steps: ITO layer deposition, ITO layer annealing and ITO film consolidation. The different steps are illustrated in figure 1.

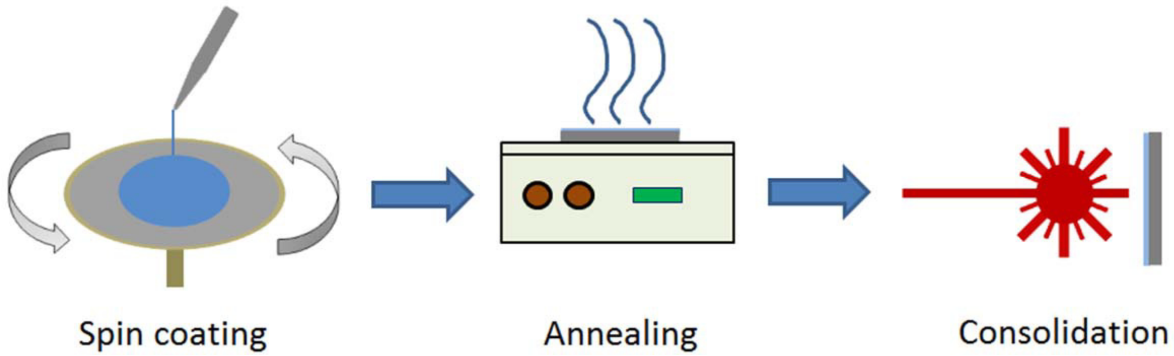

Fig. 1. Different steps in the treatment of the ITO layer.

The layers investigated in this work were deposited by spin coating. In the first step, 200 µl of the ITO suspension were deposited on a 25 mm x 25 mm x 1 mm soda lime glass substrate. Then, the substrate was spun at 3000 rpm for 20 sec. In the end a film with a thickness of 624 nm ± 58 nm was obtained. In the following the samples were annealed on a hotplate in ambient air at 450 °C for 30 min. This temperature was far below the melting point of ITO of about 1900 °C but high enough to decompose the stabilizer 2-[2-(2-methoxy-ethoxy)ethoxy]acetic in order to optimize the contact between the particles.

For particle layer consolidation a Lambda Physik LPX 315i KrF excimer laser with a wavelength of 248 nm, a maximal pulse energy of 0.8 J, a pulse length of 30 ns and a raw beam size was 15 mm x 30 mm was used. The raw beam size was limited to 5 mm x 20 mm by an aperture to cut off the inhomogeneous regions at the border of the beam. The aperture was placed in a distance of 125 mm away from the exit aperture of the excimer laser and the sample was arranged at a distance of 700 mm to the exit aperture of the laser. To determine the damage threshold at different stages of consolidation, various samples were consolidated under different conditions. Sets of two samples were consolidated by single laser pulses of 117.8 mJ/cm^2, 104.4 mJ/cm^2, 93.3 mJ/cm^2, 80.0 mJ/cm^2 and 51.1 mJ/cm^2. SEM images of the different types of layers are shown in figure 2. We refused to show an image of the spin coated layer, because spin coated and annealed layer show the same appearance in SEM microscopy.

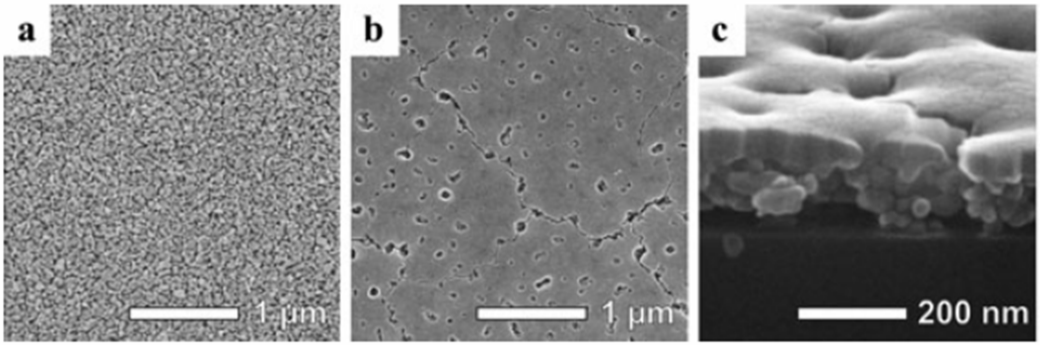

Fig. 2. (a) SEM image of the top view of an ITO layer after annealing; (b) SEM image of the top view of an consolidated ITO layer after irradiation of a single laser pulse with a fluence of 40 mJ/cm^2; (c) SEM image of the cross section of a consolidated particle layer. Images published by Baum et al.

2.3. Measurement of the damage threshold

To characterize the damage threshold of the generated layers for ultra-short pulse laser irradiation a femtosecond laser (Coherent Vitesse) was used. The system provides a laser beam with a wavelength of 800 nm, a pulse length of 100 fs, a repetition rate of 1 kHz and an average power of up to 4 W. The raw beam was focused by a lens with a focal length of 100 mm. The beam power was modulated by a polarizing attenuator. We arranged the sample in the focal plane of the lens and moved the sample in x- and y-direction using a linear stage system PLS-85 (PI|Micos).

The three-dimensional structure of the ablated regions was characterized by a laser scanning microscope (OLYMPUS Lext OLS4000). Three ablation craters were evaluated at each fluence. An example of the ablation structures is shown in figure 3. The diameter of the damaged surface was characterized in two orthogonal directions cutting the middle of the crater.

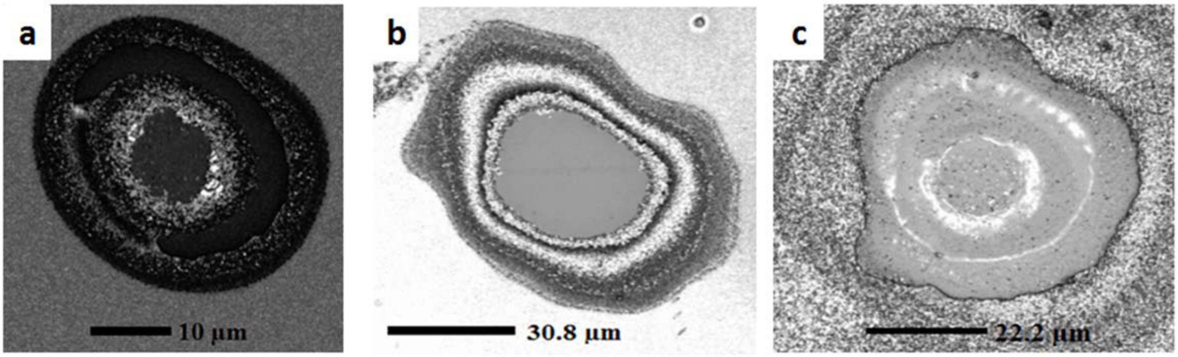

Fig. 3. laser scanning images of (a) the surface of an un-annealed film after laser treatment (single pulse at a peak fluence of 3.1 J/cm^2); (b) the surface of an annealed film after laser treatment (single pulse at a peak fluence of 14.6 J/cm^2); (c) the surface of a consolidated layer (single pulse at a peak fluence of 8.4 J/cm^2) after laser treatment (single pulse at a peak fluence of 117.8 mJ/cm^2).

2.4. Evaluation of the laser damage threshold

J. M. Liu (1984) proposed how the damage threshold of a particular material can be characterized for pulsed lasers. In this method the laser beams intensity is assumed to possess a Gaussian distribution. The energy distribution F(r) of a Gaussian beam is dependent on the radius r, the beam radius w_0 and the peak fluence F_0:

$$F(r) = F_0 e^{-2\frac{r^2}{w_0{}^2}} \tag{1}$$

Due to (1) the threshold fluence F_{th} equals

$$F_{th} = F_0 e^{-2\frac{r_{th}{}^2}{w_0{}^2}}. \tag{2}$$

In the experiment the diameter D of the damaged area was measured. The diameter of the damage threshold D_{th} of the damaged area can be derived from (2):

$$D_{th}^2 = 2w_0^2\, ln(F_0) - 2w_0^2 ln(F_{th}) \tag{3}$$

Considering the pulse energy E_P of the Gaussian beam we conclude from equation (3):

$$D_{th}^2 = 2w_0^2\, ln(E_P) - 2w_0^2 ln\left(\frac{F_{th}\,\pi w_0^2}{2}\right) \tag{4}$$

To determine the damage threshold, we substitute the equation (4):

$$D_{th}^2 = Aln(x) + B \tag{5.1}$$

$$A = 2w_0^2 \tag{5.2}$$

$$B = -2w_0^2 ln\left(\frac{F_{th}\pi w_0^2}{2}\right) \tag{5.3}$$

If the diameter of damaged area is plotted versus logarithmic, according to equation (5.1) the damage threshold can be characterized by logarithmic extrapolation. The intersection of the regression line with the horizontal axis marks the threshold damage fluence F_{th}.

Three structures, which were characterized by the laser scanning microscope, were analyzed for each fluence. Each structure provides a damage diameter in x-direction and one in y-direction. The six resulting diameters were used to calculate six threshold fluences. The average damage threshold was the mean of the six individual measurements and the error of the average damage fluence is constituted by the standard deviation of the six individual measurements.

3. Experimental results

The average laser induced damage threshold of non-annealed samples was determined to be 0.31 J/cm^2 ± 0.05 J/cm^2. For annealed layers an average damage threshold of 0.63 J/cm^2 ± 0.12 J/cm^2 was measured. Figure 4 shows exemplary the damage threshold measurement of a spin coated layer, an annealed layer and a consolidated layer.

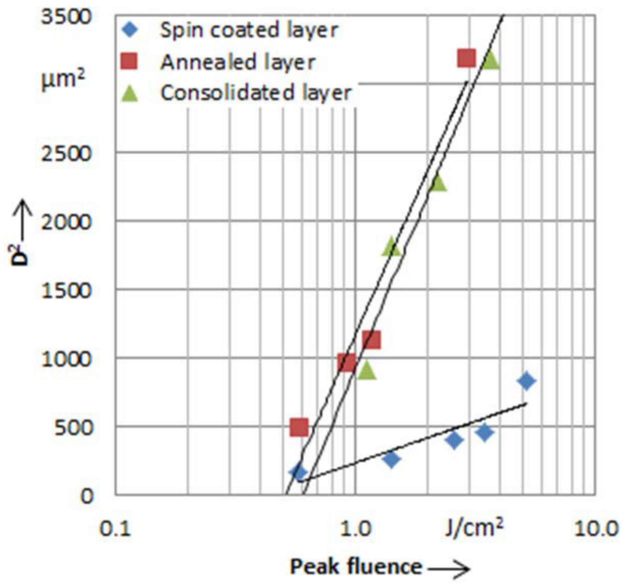

Fig. 4. Characterization of the damage threshold of a non-annealed, an annealed and a consolidated layer (consolidation was achieved by a single pulse at a wavelength of 248 nm, 30 ns with a peak fluence of 104.4 mJ/cm^2) induced by a single pulse with various peak fluences.

Figure 5 shows an example for the damage threshold of layers consolidated at different layer fluences (excimer). The average laser damage threshold of consolidated layers was determined to be 0.62 J/cm^2 ± 0.14 J/cm^2.

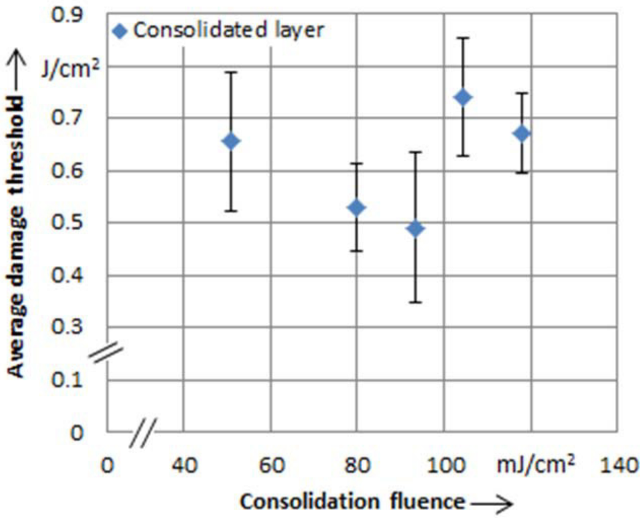

Fig. 5. Average damage thresholds of ITO layers consolidated with different fluences.

4. Conclusion

In this work we analyzed the damage threshold of different types of ITO layers. We found non-annealed layers display a lower damage threshold than annealed layers. Laser radiation induces an instantly degeneration of the organic agent which leads to an abrupt expansion in the volume of the decomposition products carrying away the surrounding particles. By annealing to heating above its evaporation temperature, the organic stabilizer is decomposed and the products are removed slowly from the layer. This leads to an increase of the damage threshold from 0.31 J/cm^2 for a non-annealed layer to 0.63 J/cm^2 for an annealed layer. In the following we characterized the damage threshold of consolidated layers. It turned out that varying the level of consolidation did not significantly chance the damage threshold of the layer. The average laser induced damage threshold of the consolidated layer was 0.62 J/cm^2. Consequently consolidation of a particulate ITO layer has no significant effect on the laser induced damage threshold compared to the damage threshold of annealed layer. The ITO layers under consolidation are about 624 nm thick, whereas the consolidated part of the particle layers is about 50 nm thick. ITO particles strongly absorb the wavelength of 248 nm using for consolidation. The penetration depth of the laser beam is very shallow and leads to a consolidation of the nanoparticulate ITO layer at the surface. Baum et al. (2013) simulated the behavior of a ZnO nanoparticulate layer in the consolidation process, which is comparable to present ITO layers in the term of absorption properties. Consequently only about 8 % of the total volume was transformed into a consolidated layer. We estimate that the consolidated layer was too thin compared to the total layer thickness to have a significant effect on the layer damage threshold. In our future work we will gradually reduce the thickness of the ITO layer on the glass substrate. For each step we repeat the damage threshold measurement to determine whether the consolidation has an effect on the damage threshold. Reducing the thickness of the ITO layer will enhance the properties of the consolidated areas in terms of the damage threshold increasing the ratio of consolidated volume compared to the whole particulate film. If consolidation has an effect on the damage threshold we expect a segregation of the values of the damage threshold depending on layer thickness of the layer and level of consolidation.

The thickness of the ITO layer influences the damage threshold of the film. S. Rung et al. (2014) investigated the effect of the layer thickness on the laser induced damage threshold of ITO films using nanosecond laser radiation. The damage threshold of an ITO layer is decreasing when the film thickness is less than the optical absorption length of the film. In this case the laser radiation is absorbed completely by the entire layer. If the optical absorption length exceeds the thickness of the ITO film the ablation threshold is increasing with the layer thickness. S. Rung attributed this behavior to a reduction in the volumic power density. In the event that the optical absorption length matches the layer thickness the damage threshold reaches its minimum. We estimate the optical absorption length of our particulate ITO layers to be 50 µm at a wavelength of 800 nm. Consequently we expect a decline of the laser induced damaged threshold reducing the thickness of the ITO layer in our following experiments.

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